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EPR and IR spectral studies of the sea water mussel *Mytilus conradinus* shells

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Abstract

The electron paramagnetic resonance (EPR) and infrared (IR) spectral studies have been employed on the periostracum, the prismatic layer and the nacre of the shell of the marine bivalve molluscan *Mytilus conradinus* of the South Indian origin. All the layers of this shell show Fe^{3+} ion spin resonance signals in common. The inner layer namely nacre at room temperature shows EPR signals of Fe^{3+} ions and the heated one exhibits a sextet hyperfine pattern characteristic of Mn^{2+} ions. The prismatic layer of the shell also exhibits a similar spectrum, but of distinct pattern. The spin-Hamiltonian parameters have been evaluated for the prismatic and nacreous layers of this shell. Infrared spectra of the two main layers of the shell namely prismatic and the nacre exhibit the characteristic bands of CO_3^{2-} molecular ion in different symmetries of CaCO_3 . © 2000 Elsevier Science B.V. All rights reserved.

Keywords: EPR; IR spectra; Transition metal ions; CaCO_3 lattices; Sea shells

1. Introduction

Spectral investigations of carbonate minerals are very useful in solving the sedimental petrology problem of Mn^{2+} concentration and its distribution between non-equivalent positions within the corresponding mineral structure, as produced by the mineral crystallization and evolution. EPR studies of various fossil fuel sources have disclosed, besides organic free radicals, various metal ions (Mn^{2+} , Fe^{3+}) and porphyrin-bound VO^{2+} .

Naturally occurring marine materials deposited by the various molluscs examined consist, accord-

ing to their spectral investigations, two common mineral forms of CaCO_3 , either aragonite or calcite and in some cases are composed of both materials. Sea shells are composed of 97–99% CaCO_3 (calcite, aragonite or vaterite) with lesser amounts of MgCO_3 , $(\text{Al}, \text{Fe})_2\text{O}_3$, SiO_2 , $\text{Ca}_3\text{P}_2\text{O}_8$, CaSO_4 , protein and mucopolysaccharides [1–5]. In addition to these major and minor constituents, trace amounts of Sn, Mo, Mn, Cd, Ti, B, Pb, Au, Ag, Ni, Co, Bi, Cu, Sr, Rb and As have also been found in varying amounts [6]. Aragonite shells and aragonitic mineral deposits are known to undergo slow metamorphism into calcite [7,8].

The crystal structure of calcite and aragonite has been extensively studied and referenced elsewhere [5,9–11]. The crystal structure reveals that

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the Ca^{2+} sites in calcite have localised D_{3d} symmetry with a six nearest neighbour oxygen atoms, whereas the Ca^{2+} site in aragonite has nine nearest neighbour oxygen atoms with C_s symmetry. While Blanchard and Chasteen [12] observed that Mn^{2+} ions are in D_{3d} symmetry, White et al. [7] observed the Mn^{2+} ions in C_s symmetry. Nagaraja Naidu et al. [9] studied the EPR spectra of Mn^{2+} ions present in the fresh water mussel *Lamellidens marginallis* shells and reported the aragonitic (C_s) structure of the shells. Douifi et al. [10,11] have studied the ESR spectra of Mn^{2+} ions and the CO_2^- radicals in irradiated marine shells and reported both aragonite and calcitic forms. Since no EPR observations have been done for the shells of Indian sea mussel *Mytilus conradinus* (hereafter to be referred to as MCS), the authors have taken up the present investigation.

The *Mytilus* is marine sedentary, cosmopolitan and found attached to the rocks between tide marks. It belongs to the class of Lamellibranchia [13]. The *M. conradinus* shell is thin; roughly semicircular, elongated, equivalved, umbo sharp, terminal, having anterior teeth near the umbo. Anterior mussel impressions are small, placed near the margin. The mytilus bivalve shell consists of three layers; the outer layer of the shell namely periostracum consists of mainly quinone tanned protein. The deep brown crystalline layer just beneath the periostracum is the prismatic region which contains unique-prisms of calcite [14] and the layer further below prismatic region is the nacre, consisting of crystals arranged in neatly packed horizontal rows.

2. Experimental

The samples of the fresh sea mussels of *M. conradinus* were collected from the south Indian coast. The soft parts inside were removed after opening the bivalve of the shell. The valves were cleaned and dried. The three layers of the valve were separated out as follows; the outer layer periostracum was easily removed as it is a layer composed of the organic material quinone tanned protein. The inner layer namely nacre was collected carefully from scratching the strong pris-

matic layer. To avoid any part of nacre and periostracum content in prismatic layer, the prismatic layer has been polished well on either side before powdering. The EPR spectra of these powdered samples were recorded on a JEOL FE 1X ESR spectrometer operating at X-band frequency and 100 kHz modulation. The temperature variation EPR studies were performed by using a JES-UCT-2AX variable temperature controller. Samples for infrared analysis were prepared by KBr pellet technique, in which the powdered sample was mixed with dried KBr and pressed into a pellet. The infrared spectra have been recorded on a Bruker-IFS 66V FT-IR spectrophotometer, at RSIC, Indian Institute of Technology, Madras, India.

3. Results and discussion

Preliminary chemical analysis shows the presence of Mn and Fe metals in traces in the *M. conradinus* shells. Five samples of MCS were taken for the EPR studies. All of them show similar spectral pattern except a very slight variation in intensities of their respective spectra.

3.1. EPR spectra of the *M. conradinus* shells

3.1.1. Periostracum

The EPR spectrum of the periostracum layer at room temperature (RT) shows a sharp resonance line at $g = 2.028 \pm 0.002$ having a linewidth $\Delta B_{pp} = 14$ gauss and also a weak resonance signal at $g \approx 4.1$. It is known that the periostracum consists of mainly quinone tanned protein [15,16]. The resonance at $g \approx 2.0$ is expected due to this radical, but the sharp signal is overlapped on either side by a broad signal. The broad signal is due to Fe^{3+} ions. This can be judged well from the spectrum recorded in low range scaling (± 1000 gauss) which is not shown here. As the temperature of the periostracum is lowered to 103 K, the intensity of the $g \approx 4.1$ resonance line, increases and it has a linewidth of $\Delta B_{pp} = 90$ gauss. Fig. 1 shows the EPR spectra of Periostracum at 300 and 103 K. From the spectrum, the two resonances at $g \approx 2.0$ and 4.1 are clearly seen.

The g values for the observed resonances indicate the presence of Fe^{3+} ions in high concentration and the observed phenomenon has been attributed to the high spin Fe^{3+} ions in orthorhombic symmetry. The presence of Fe^{3+} ion in periostracum is probably an indicative of an important role of iron in this layer [12]. In this layer no characteristic manganous signals were observed at any stage.

3.1.2. The prismatic region

No EPR signal was observed for a fresh sample of prismatic region at room temperature (RT). When the sample of prismatic region was heated at 420 K for 1/2 h, the polycrystalline EPR spectrum exhibits a hyperfine spectrum of Mn^{2+} ions (electron spin $S = 5/2$ and nuclear spin $I = 5/2$) arising from its characteristic central sextet $|\pm \frac{1}{2}\rangle \leftrightarrow |\mp \frac{1}{2}\rangle$. The reason for the non-observation of EPR spectrum at room temperature for the material of the prismatic layer may be due to the presence of manganese in trivalent state. The Mn^{3+} ion with its low spin ($S = 0$), is diamagnetic and hence becomes an EPR silent one. It is known that manganese oxidation–reduction is a common chemical reaction taking place in natural soil bioprofiles usually caused by climatic changes [17]. During the chemical weathering manganous

species might be oxidised to manganic ones. When the sample is heated, a reaction may take place trapping an electron to form the Mn^{2+} ion. Similar observation was assigned in case of the EPR study of CaCO_3 crystals by Low and Zeira [18].

Fig. 2 shows the EPR spectrum of the polycrystalline sample of the prismatic region. The spectrum consists of two sets of $\Delta M_I = 0$ allowed hyperfine lines ($1/2, m \leftrightarrow -1/2, m-1$, for $m = 5/2, 3/2, 1/2$) of Mn^{2+} ions. In between each transition, forbidden doublets ($\Delta M \neq 0$) were also seen. Besides this, the resonance line located at $g \approx 2.0$ has also been observed. This signal may be either due to the trace concentrations of CO_2^- molecular-ion [19] or due to Fe^{3+} ion as the observed linewidth for $g \approx 2.0$ signal, $\Delta B_{pp} \approx 6$ gauss is a little higher than the expected characteristic Mn^{2+} signal. As one expects a broader resonance line for the signal at $g \approx 2.0$, for Fe^{3+} ions, the observed linewidth (≈ 6 gauss) suggests that the resonance signal at $g \approx 2.0$ is due to CO_2^- ion, but not due to Fe^{3+} ions. Hence one can safely assign this signal due to the CO_2^- . The observation of slightly broadened Mn^{2+} resonance spectrum may be expected due to the exchange coupling between the paramagnetic species. Similar observations were also reported in case of Mn^{2+}

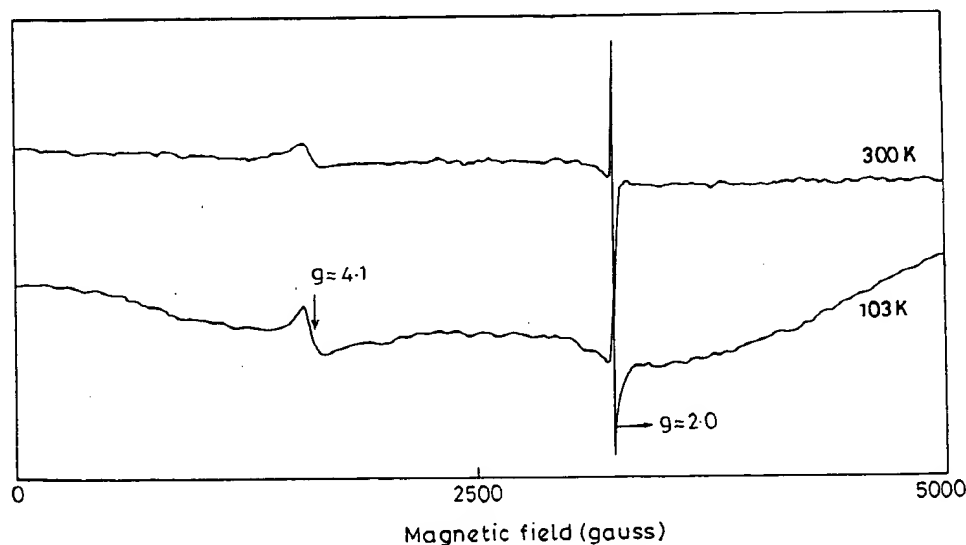


Fig. 1. X-band EPR spectrum of periostracum of the *M. conradinus* shell at 300 and 103 K.

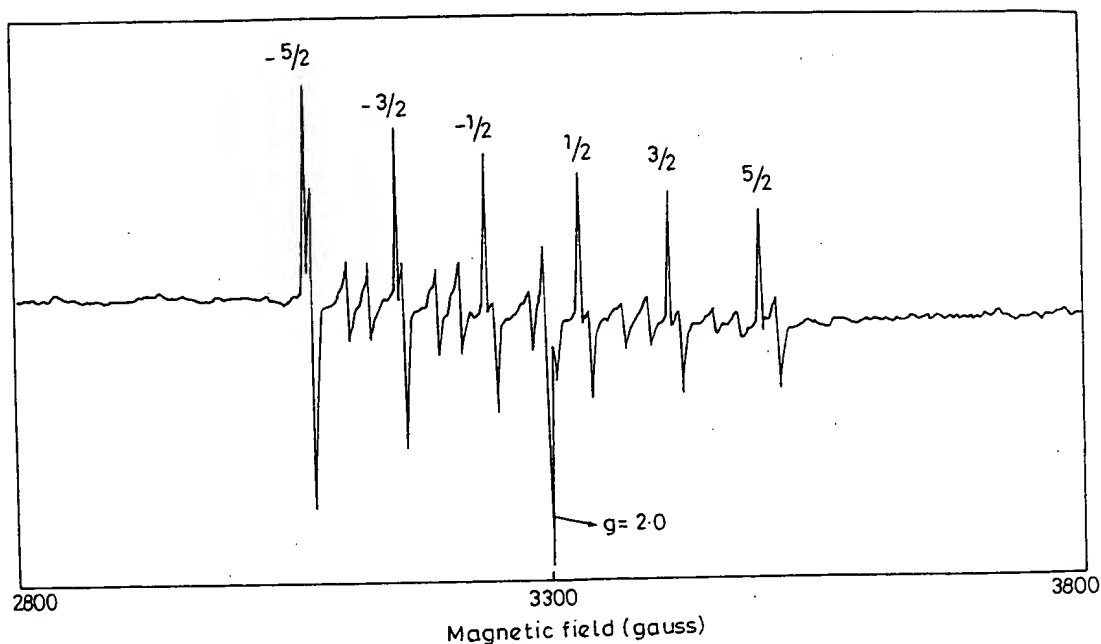


Fig. 2. X-band EPR spectrum of polycrystalline (heated at 420 K) sample of the prismatic layer of the MCS shell. The numbers shown above the peaks are the corresponding m_I values of Mn^{2+} spectrum.

spinel [20–22]. This can be judged well by recording the EPR spectra at different temperatures. If it were due to the exchange coupling, the linewidths should not change invariably except a variation in intensities and slightly in its g values [23]. The EPR spectrum was recorded at different temperatures, but no significant variation in linewidths was observed, but a remarkable variation in intensities has been observed.

The observed EPR spectrum can be explained by the spin-Hamiltonian of the form [24]

$$H = \beta B g S + D(S_z^2 - S(S+1)/3) + SA I \quad (1)$$

where the symbols have their usual meaning.

From the observed transition ($M = |\pm 1/2\rangle \leftrightarrow |\mp 1/2\rangle$), the g and A parameters were calculated for the polycrystalline spectrum of the prismatic layer and are given in Table 1. For powders which are isotropic to first order perturbation, the zero-field splitting parameter D has been evaluated by the procedure given by Bleaney and Rubins [25]. The D values are in close agreement with those obtained for Mn^{2+} in calcitic lattices reported in literature [7,12,26]. From the

intensity variations of the hyperfine lines observed for the central sextet, the anisotropy of hyperfine splitting constant may be expected [22]. In the present case as is seen in Fig. 2, the intensity variation from $m_I = \pm 5/2$ to $m_I = \pm 1/2$ shows that A is much anisotropic in the prismatic region of the shell. The intensity variation is also a contribution due to the zero-field splitting parameter.

Table 1

The spin-Hamiltonian parameters (g , A and D) for Mn^{2+} ions in prismatic and nacreous layers of the sea shell *M. conradinus*

| Shell layer | $g \pm 0.001$ | $A \ 10^{-4}$ $cm^{-1} \pm 1$ | $D \ 10^{-4}$ $cm^{-1} \pm 1$ |
|-----------------|---|--|----------------------------------|
| Prismatic layer | $g_z = 2.000$ $g_x = g_y = 1.998$ | $A_z = 83$ $A_x = A_y = 81$ | -90 |
| Nacreous layer | $g_z = 1.999$ $g_y = 1.997$ $g_x = 1.992$ | $A_z = 79$ $A_y = 78$ $A_x = 75$ | |

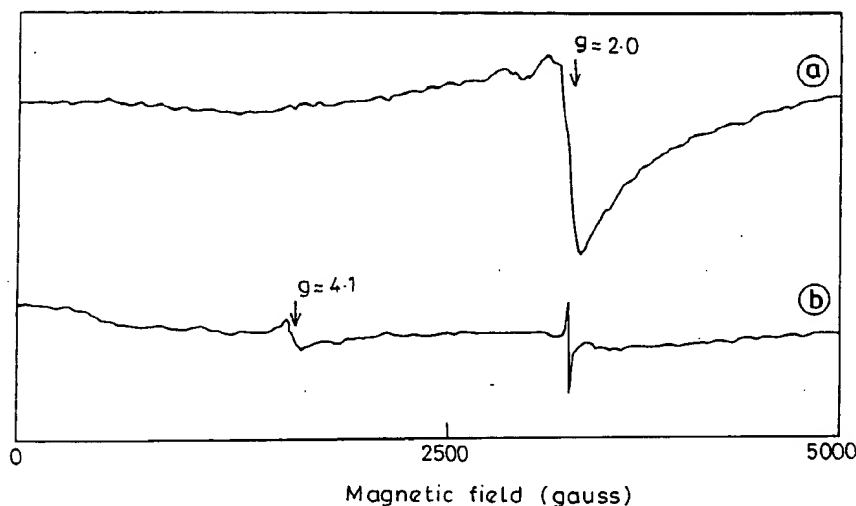


Fig. 3. X-band EPR spectrum of, (a) single oriented section of a fresh nacre sample at room temperature; (b) polycrystalline nacre sample of the MCS at 113 K.

3.1.3. The nacreous layer (or the mother of the pearl)

At room temperature, a single oriented section of a fresh nacre exhibits only an intense resonance at $g \approx 2.0$ and is shown in Fig. 3. This is due to the presence of Fe^{3+} ions, and this in fact, indicates that the microcrystallites of this region possess polycrystalline nature. The EPR spectrum for a fresh sample of nacre recorded at 113 K is also shown in Fig. 3. This spectrum exhibits two resonances with a sharp resonance line at $g \approx 2.0$ and the another at $g \approx 4.1$ with a linewidth $\Delta B_{pp} = 75$ gauss. The resonance line at $g \approx 4.1$ can be attributed to the Fe^{3+} ions in rhombic symmetry [27].

The nacre was heated above 800 K for 1 h and powdered. The EPR spectrum of the polycrystalline sample of heated nacreous layer at room temperature shows a well resolved Mn^{2+} hyperfine sextet belonging to $|\pm 1/2\rangle \leftrightarrow |\mp 1/2\rangle$ transition and is shown in Fig. 4. The spectrum is physically distinct to that of prismatic region shown in Fig. 2. In Fig. 4, the narrow lines correspond to the Mn^{2+} ($S = I = 5/2$) hyperfine central sextet transition with $A = 84$ gauss and a broad signal centred in between the Mn^{2+} sextet having a linewidth $\Delta B_{pp} = 50$ gauss is also seen. The same heated specimen of this layer preserved

at room temperature for a long time did not show any characteristic Mn^{2+} EPR spectrum at normal conditions. This may be due to the time decay during which the oxidation occurs in case of the manganese ions and becomes EPR silent (Mn^{3+}) ions.

The Mn^{2+} ion central hyperfine sextet spectrum observed in the nacreous region can be explained by the spin-Hamiltonian given in Eq. (1). The spin-Hamiltonian parameters were evaluated and are included in Table 1. The D value has been calculated from the forbidden transition lines of the spectrum. The values are in close agreement with those of the aragonitic lattices reported in literature [7,28]. However a decrease in the D value of nacreous layer of the shell lattice than those of other aragonite lattices reported in literature may be due to the presence calcitic material in this layer as an untransformed one and this is confirmed from the infrared spectra which is discussed in the latter section. As the temperature is lowered, the Mn^{2+} spectrum slowly vanishes, and at 113 K, the Mn^{2+} hyperfine spectrum completely disappears and a broad signal centred at $g \approx 2.0$ remains. This may be due to the presence of iron ions relatively higher in concentrations in this layer than that of the manganoous ions, thus resulting in the broad-

ening of the Mn^{2+} EPR linewidths. This is expected due to the dipolar interactions of Mn^{2+} ions with paramagnetic iron ions, modulated by spin-lattice relaxation of the later ions [23,29]. The broader resonance component at $g \approx 2.0$ can be attributed to the magnetically coupled Fe^{3+} ions [30].

In evaluating the zero-field splitting parameter (D) and the hyperfine splitting constant (A), we considered the sign of the hyperfine splitting constant A , as negative since for Mn^{2+} ions, A value is always negative [23,31]. In an earlier EPR work on Mn^{2+} ions in CaCO_3 lattices, a negative sign was assigned for the D value [26]. The same sign has been adopted in the present case. On comparison of the D and A values of the two layers of the MCS with the other shells reported in literature, it is known that the nacreous layer compare well with

the aragonite type lattices [7,9] and those of the prismatic layer with the calcitic type [7,12] lattices.

The detailed inspection of polycrystalline spectra of the heat-treated nacre specimen to that of the prismatic layer shows the following features; (i) in nacreous specimen, a distinct EPR spectrum with a slightly different spacings in the hf lines and the forbidden doublets have been observed. (ii) Fe^{3+} ions are present in a relatively higher concentrations, (iii) the characteristic Mn^{2+} EPR spectrum of the nacreous layer disappears at low temperatures, whereas no significant change is observed in the EPR spectra of the prismatic one. From the above features, it can be concluded that the material of the prismatic and nacreous layers are of different forms of symmetry, characteristic of calcite and aragonite [18] respectively. The values of the zero-field splitting parameter (D) for both the specimen further supports this conclusion.

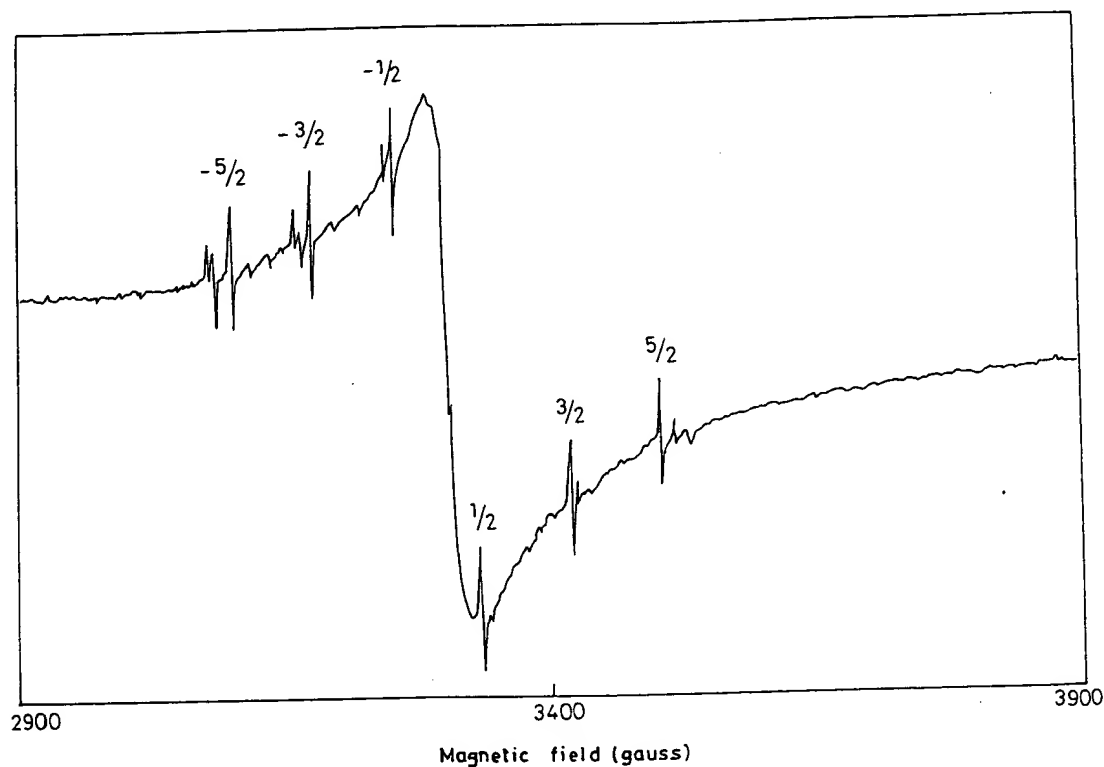


Fig. 4. Polycrystalline X-band EPR spectrum of nacre sample of MCS at room temperature (after heating it at 800 K and cooled to room temperature). The numbers shown above the peaks are the corresponding m_l values of Mn^{2+} spectrum.

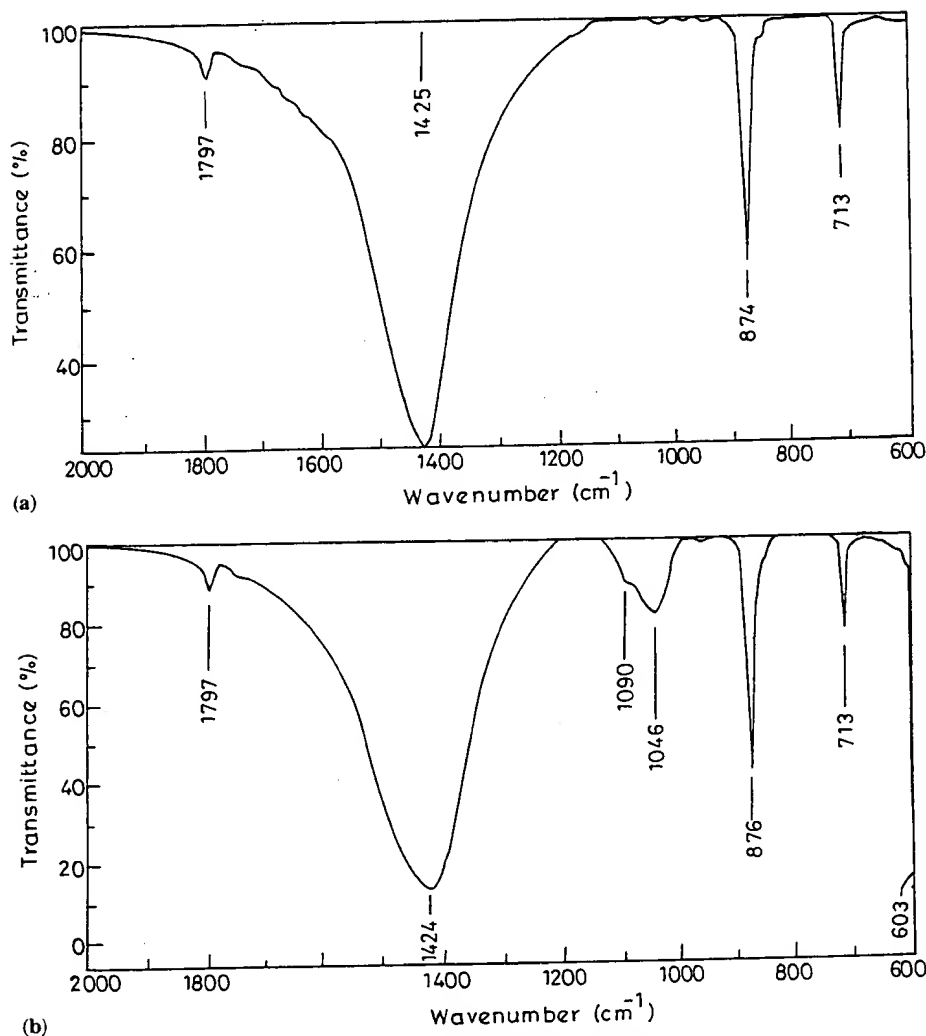


Fig. 5. (a) FT-IR spectrum of prismatic layer of the MCS shell; (b) FT-IR spectrum of the nacreous layer.

3.2. Infrared spectral studies

Considerable amount of efforts have been devoted to the study of CaCO_3 relating the infrared absorption bands to various vibrational motions and orientation of the carbonate ion [32–35,41]. In this section, the results on the infrared spectra of the prismatic and nacreous layers of the *M. conradinus* shells have been discussed.

A molecular ion like CO_3^{2-} , belonging to a point group D_{3h} in a lattice exhibits generally, four normal modes of vibration [36], the frequen-

cies correspond to a symmetric stretching, $\nu_1(A_1)$; an out-of-plane bending $\nu_2(A_2)$; a doubly degenerate asymmetric stretching $\nu_3(E)$; and a doubly degenerate planar bending $\nu_4(E)$. As the symmetric vibration $\nu_1(A_1)$ is reported to be infrared inactive, hence only three fundamentals are ordinarily observed.

The FT-IR spectra of the prismatic and nacreous layers of the *M. conradinus* shell are shown in Fig. 5(a) and (b), respectively. In Fig. 5(a), of the prismatic layer, three prominent bands of CO_3^{2-} were observed. In this spectrum, the intense sharp band at 876 cm^{-1} has been assigned

to $\nu_2(A_2)$ mode, the out-of-plane deformation band, which is infrared active [37]. The broad band with halfwidth $\approx 195 \text{ cm}^{-1}$ centred at 1424 cm^{-1} is assigned to $\nu_3(E)$ mode of CO_3^{2-} ion and is conformably of the CaCO_3 material. The band at 713 cm^{-1} in this layer corresponds to $\nu_4(E)$ in-plane deformation. The absence of the infrared inactive mode, $\nu_1(A_1)$ in prismatic layer suggests that there is no breakdown of symmetry to that of free CO_3^{2-} radical and thus an indicative of the D_{3h} symmetry corresponding to the calcitic form of the CaCO_3 .

In the infrared spectra of nacreous layer as shown in Fig. 5(b), it is observed that all major IR bands of prismatic layer as shown in Fig. 5(a) have corresponding bands in that of the nacre, except the presence of a few additional bands. It is known that only minor changes in the infrared frequencies might be produced by changes in the environment of the CO_3^{2-} ion [36]. The band at 1090 cm^{-1} in the infrared spectrum of nacreous layer, corresponds to $\nu_1(A_1)$ fundamental mode of the CO_3^{2-} molecular ion in aragonite group [38,39]. The presence of the $\nu_1(A_1)$ mode in the infrared spectrum of nacre suggests that the structural change in the transformation from calcite to aragonite of the nacreous layer is sufficient to activate this mode. This is in good agreement with the expected ν_1 mode of aragonite symmetry. The band at 1046 cm^{-1} may be due to some other mineral composite expected to have filled inside with the surrounding sediments in this bivalve. From the observed intensity and the position, the band at 1046 cm^{-1} may be attributed to the silicate impurity [39]. The broad band at 1424 cm^{-1} which differs in absorption with a halfwidth $\approx 155 \text{ cm}^{-1}$ is an indicative of aragonite and the presence of the absorption band at 1090 cm^{-1} in the higher wavelength side is sufficient to confirm this. The variation in the absorption of this band over the calcite can be related to the intergrowth of aragonite and calcite. From these observations one may safely confirm that the major constituent in this layer is the aragonite material rather than the calcite. The presence of calcitic material in this aragonitic nacre supports that there is an important role of transfer of calcium to the mussel tissue from its surroundings.

Besides this, the FT-IR spectrum consists of a weak band at 603 cm^{-1} , which may be due to the CO_2^- radicals, which were not exhibited in the infrared spectrum of the calcitic prism. The bands observed at 1797 and 2515 cm^{-1} are in good agreement with the bands observed for CO_3^{2-} in CaCO_3 lattices reported in literature [40].

4. Conclusions

1. The detailed EPR analysis of the molluscan shells *M. conradinus* (MCS) shows the presence of iron and manganese ions in traces.
2. The presence of EPR signals in periostracum and nacreous layers at $g \approx 4.1$ have been attributed to Fe^{3+} ion in rhombic symmetry.
3. For the fresh sample of *M. conradinus* shells, no Mn^{2+} EPR signals were observed, and the heated sample exhibits well defined Mn^{2+} EPR signals and this has been attributed to the electron capture from the EPR silent trivalent manganese to the active manganic ion.
4. From the characteristic EPR spectral data of Mn^{2+} ions of the *M. conradinus* samples, it is found that the prismatic and nacreous layers exhibit calcitic and aragonitic nature respectively.
5. The infrared spectra of the prismatic and nacreous layers exhibit characteristic bands of CO_3^{2-} molecular ion in different symmetries.

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